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Facile Fabrication, Characterization of Bismuth Vanadate Nanoparticles Via Hydrothermal Method and Its Photocatalytic Properties

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ABSTRACT

Bismuth vanadate ($BiVO_4$) photocatalyst with nanoparticles morphologies were prepared by a facile hydrothermal process with bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) and ammonium vanadate (NH_4VO_3) were used as the starting precursors. The physical and photophysical properties of the as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), infrared spectroscopy (IR), and UV–Vis diffuse reflectance spectroscopy (UV–Vis-DRS) for investigate the phase, morphology, particle size, elemental composition. It is shown that the $BiVO_4$ is constructed of numerous of nanoparticles and well defined morphology. UV-vis spectrum is used to estimate the band gap energy of the prepared BiVO4 which showed narrower bandgap energies. The photocatalytic activities of the $BiVO_4$ materials were evaluated for the degradation of Rhodamine blue (RhB) under visible-light irradiation.

Keywords: Bismuth vanadate, precursors, light irradiation, morphology.

INTRODUCTION

Semiconductor photocatalysis is one of the most promising technologies for solar energy utilization and environmental remediation.[1] TiO_2 has been proven to be photocatalytically active for the degradation of organic pollutants.[2] However, TiO_2 responds only to ultraviolet light, which represents a small fraction (ca. 4%) of the sunlight energy. Therefore, it is highly required to develop visiblelight-driven photocatalytic materials.

As one of the Ti-free semiconductor photocatalysts, bismuth vanadate has recently attracted much attention due to its interesting technological properties, such as ferroelasticity[3-].[4] ionic conductivity.[5] and strong photocatalytic effect on water splitting and organic pollutant decomposing under visible light irradiation.[6-8] $BiVO_4$ with nanoparticle sizes and morphologies showed good photocatalytic performance for the degradation of Methylene Blue[.9] under visible-light illumination. In this work, we report the fabrication, characterization and photocatalytic properties of highly crystalline monoclinic $BiVO_4$ nanoparticles with nano structures for the degradation of Rhodamine Blue (RhB) under visible-light.

1. EXPERIMENTAL

1.1 Catalyst fabrication

The $BiVO_4$ catalysts were fabricated by adopting the hydrothermal strategy with the typical procedure was as follows: 2:1 ratio of well-ground $Bi(NO_3)_3 \cdot 5H_2O$ and NH_4VO_3 powders were dissolved in 50 mL of HNO_3 aqueous solution (2 mol/L) under stirring. The mixture was transferred into a 100-mL Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 12 hr. The as-obtained yellow precipitate was in turn filtered, washed with deionized water, dried at 60 °C for 12 hr, and calcined at 550 °C for 4 hr in a muffle furnace, thus generating the $BiVO_4$ catalyst. All of the chemicals were purchased from Merck chemicals and used without further purification.

1.2 Catalyst characterization

X-ray diffraction patterns of the $BiVO_4$ samples were recorded on an X-ray diffractometer (Bruker/AXS D8 Advance, Germany) with a Cu *K*α X-ray irradiation source (λ = 0.15406 nm). Morphologies of the sample particles were determined on a scanning electron microscopic (Gemini Zeiss Supra 55, Germany) operated at 10 kV. Infrared spectra (IR) of the samples were recorded by (Jasco) analyzer. The ultraviolet-visible (UV-Vis) diffuse reflectance spectra of the samples were recorded on a Shimadzu UV-2450 spectrophotometer (Japan) using $BaSO_4$ as standard.

1.3 Photocatalytic evaluation

Photocatalytic activities of the $BiVO_4$ samples were evaluated for the degradation of Rhodamine Blue (RhB) as model a organic pollutant under visible-light illumination in a quartz reactor. A 300-W Xe lamp was used as light source and an optical cut-off filter was employed to only permit the illumination of light with wavelength of > 400 nm. The photocatalytic evaluation experiments were performed at

ambient temperature as follows: 0.1 g of the $BiVO_4$ sample was added to 100 mL of RhB solution, after being ultrasonicated for 0.5 hr and magnetically stirred for 3 hr to reach the adsorption-desorption equilibrium. The temperature of the reaction system was kept at ca. 20 °C using flowing cool water. A small amount (4 mL) of the reactant solution was taken at 30-min intervals and separated by centrifugation for RhB concentration determination. The RhB concentration (Ct) after a certain reaction time (t) was determined by measuring the absorbance of the reactant solution at 464 nm during the photocatalytic degradation process on the aforementioned UV-Vis equipment. The Ct/C_0 ratio was used to evaluate the photocatalytic performance of the sample.

2. RESULTS AND DISCUSSION

2.1 Crystal structure and surface area

Figure 1 shows the XRD patterns of the $BiVO_4$ samples obtained under hydrothermal conditions. All of the diffraction peaks of the $BiVO_4$ samples could be well indexed to the monoclinic (JCPDS PDF# 14-0688). The XRD pattern broad peak intensities at about 29.8 was indicative of well-crystallized $BiVO_4$ were gradually formatted. It is composed of smaller microscopic particles approximately 70 nm. No impurity peaks were observed, indicating that 180 °C is sufficient for the formation of phase-pure monoclinic $BiVO_4$ hydrothermally.

2.2 Morphology studies

The morphology and microstructure of samples were revealed from the SEM images of the $BiVO_4$ (Fig.2.). It is observed that the $BiVO_4$ samples were composed of nano particles. It showed that all primary particles with nano-sized diameter were nearly the same in size and were almost near cubic structures. Particle sizes were measured according to the statistical analysis of large number of particles, and the average diameters of particles were measured as around 55 nm. The elemental composition present in the prepared catalyst was analyzed by EDX spectrum which is shown in fig.3, the analysis report confirm with the elements present in the catalyst.

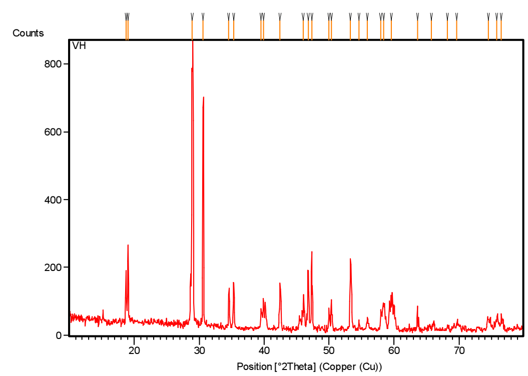

Fig.1. XRD patterns of $BiVO_4$.

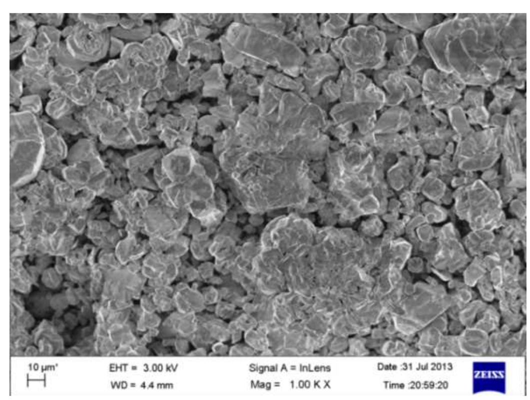

Fig.2. SEM images of $BiVO_4$

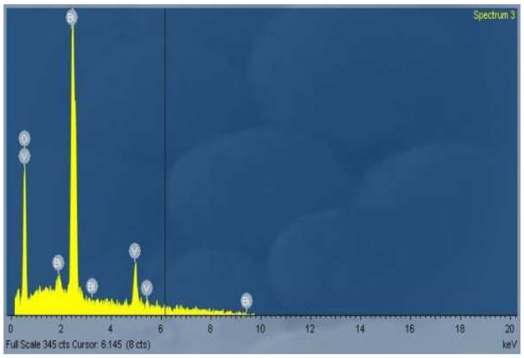

Fig. 3. SEM and EDX image of $BiVO_4$

2.3. Optical absorption behavior studies

Fig. 4 shows FTIR spectra of synthesized samples, recorded ranging from 400 to 2000 cm−1 at room temperature and shown a characteristic broad and strong IR band near 736 cm^{-1} with shoulders at 892, 828, 684 and 623 cm^{-1} it may be the wave number shift of the V–O asymmetric stretching vibration from736 to 720 cm^{-1} The tiny band near 1600 cm^{-1} can be assigned to the presence of residual trace water in the structure. According to the previous works, those IR bands corresponded to the characteristic vibrations of monoclinic $BiVO_{4.}$ [10]

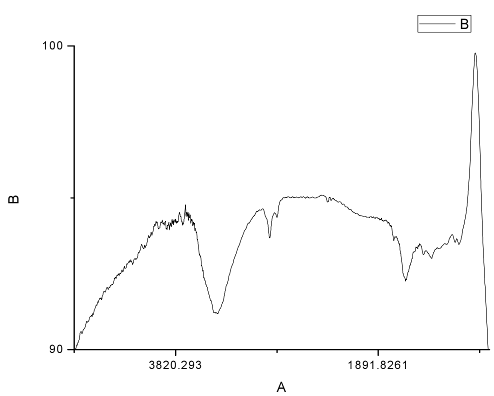

Fig.4. IR spectra of $BiVO_4$

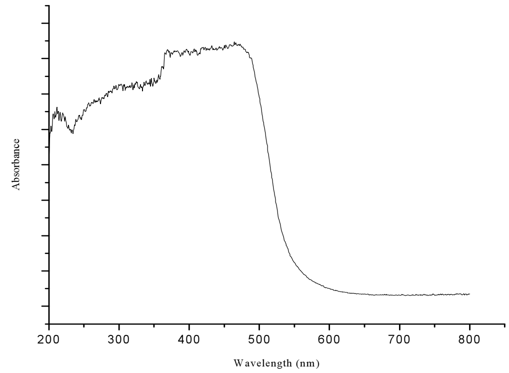

Fig.5. UV–Vis spectra of $BiVO_4$

The UV–Vis diffuse reflectance absorption spectra of the as-synthesized samples shown in fig.5. The absorption edge is at the visible-light region up to 600 nm and the samples exhibited strong absorption in the UV- and visible-light regions, which was characteristic of monoclinic $BiVO_4$.[11] The steep shape of each spectrum in the visible-light range was due to the band gap transition and the *E*g value of each $BiVO_4$ sample could be estimated from the intercept of the plot. The band gap energies of the $BiVO_4$ samples were in the range of 2.35 eV, which were comparable to those reported by other investigators[12] and the lower band gap energies, indicating that the $BiVO_4$ samples could respond to visible light more effectively and would hence be expected to show higher visible-light-driven photocatalytic performance.

2.5 Photocatalytic performance

The $BiVO_4$ photocatalytic activity was evaluated on the degradation of RhB in aqueous solution under visible-light irradiation. As shown Fig.6. The photolysis test demonstrates that the degradation rate is

higher nearly 82% after 180 min irradiation. It is indicate that the catalyst structures of $BiVO_4$ could favor the adsorption and diffusion of reactants as well as the facile accessibility of incident light to more surfaces of catalysts, thus leading to an enhancement in photocatalytic activity. The phtocatalytic result, the catalyst has the best photocatalytic activity under the irradiation of visible light.

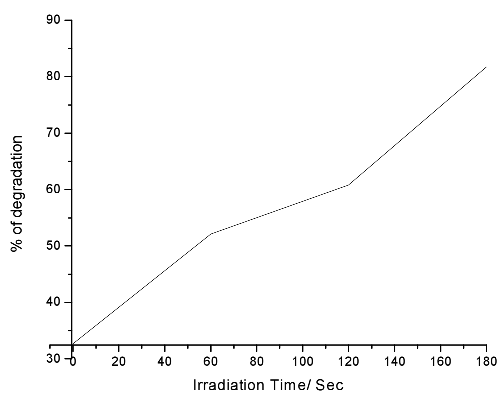

Fig.6. Photocatalytic efficiency of $BiVO_4$

3. CONCLUSIONS

A hydrothermal method was applied to synthesize nano crystalline $BiVO_4$ has been established by adding aqueous solution of solution of $Bi(NO_3)_3$ and NH_4VO_3 in HNO_3 at 180 ^0C temperature. The obtained monoclinic crystalline $BiVO_4$ nanoparticles were characterized by XRD, SEM-EDX, UV–Vis, and FTIR techniques. The results revealed that the as-prepared samples with narrow band gaps and interesting morphologies, crystallinity and particle size showed much higher photocatalytic activities for degradation of RhB and suggesting potential future applications in photocatalysis by sunlight.

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